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Zinc Sludge Recycling After Kastone Treatment of Cyanide Bearing Rinse Water

Metal Plating Corp, Connorsville, Ind

Prepared for

**Industrial Environmental Research Lab -Cincinnati, Ohio Industrial Pollution
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ZINC SLUDGE RECYCLING
AFTER KASTONE® TREATMENT OF CYANIDE-
BEARING RINSE WATER

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the pollution to our environment and to our aesthetic and physical well-being requires corrective approaches that recognize the complex environmental impact these operations have.

The Industrial Environmental Research Laboratory - Cincinnati uses a multidisciplinary approach to develop and demonstrate technologies that will rectify the pollutional aspects of these operations. The Laboratory assesses the environmental and socio-economic impact of industrial and energy-related activities and identifies, evaluates and demonstrates control alternatives.

This report is a product of the above efforts. It attempts to show the feasibility of zinc metal recovery after oxidation of cyanide by formaldehyde and Kastone®. Included is a critique of the design of necessary equipment and modifications of the plating process needed to accommodate the recovery.

It was found that the zinc sludge could be recovered. This recovery required minimizing volume of the solids, by eliminating water hardness and then utilizing filtration. There are savings which result primarily from lowered anode useage as well as the recovered zinc. Recycling is useful to metal finishers using the Kastone system where transportation cost to landfill are high. Transportation costs would be \$2,000.00 per year minimum at \$40.00 per drum of sludge. Thus those companies whose transportation costs are as large as this would benefit from recycling as an economic alternative.

Further information on the subject could be obtained from the Industrial Pollution Control Division, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

D.G. Stephan, Ph. D.
Director
Industrial Environmental Research Laboratory

ABSTRACT

The purpose of this project was to demonstrate the feasibility of reclaiming sludge. The sludge was produced by the destruction of cyanide by Kastone® in zinc-cyanide dragout rinse water. The clear supernatant was discharged to the municipal sewer and the sludge eventually recycled to the plating tank. The general approach was to transfer cyanide-bearing rinse water to the treatment tank, treat, settle, decant clear supernatant, transfer sludge for further concentration, and in one way or another return dissolved sludge to the plating tanks.

The possibilities of contaminant accumulation were present. Breakdown products, ferrocyanide, copper and other possible metallics would be returned to the plating tank. The operation at Metal Plating Corporation has two plating tanks. This allowed a control and experimental tank for evaluation. The major difficulty encountered was a precipitate mostly of calcium and magnesium hydroxides that was formed in the treatment process and does not redissolve as does the zinc oxide sludge. The presence of calcium and magnesium is known to be present in the water used. The hydroxide sludge presented mechanical problems in handling in the recycling process.

It was also found that methods used to minimize dragout minimized subsequent treatment and had a positive influence on our recycling efforts.

This report was prepared and submitted by Metal Plating Corporation under partial sponsorship of the USEPA in fulfillment of Project No. S-803265. This project was completed as of July 15, 1975.

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SECTION I

INTRODUCTION

The conventional method of treating metal finishing wastes is chemical oxidation of cyanide, reduction of chromate, and precipitation of the heavy metals. The heavy metal sludge is generally disposed of by landfill burial, which represents an economic loss to the plater and an irretrievable material loss of a non-renewable metal resource. Cyanide zinc plating is a major portion of all cyanide plating in the country, and much of the zinc metal value is lost each year by platers because the zinc metal lost in the rinse water is not recovered and reused. Large quantities of metals are similarly lost from cyanide copper, cyanide brass and cyanide cadmium plating operations. There has been no systematic plant demonstration to show that sludges produced by current destruction processes for cyanide plating wastes can be recycled to plating baths. The second problem is that as platers adopt water conservation techniques, it is expected that the concentration of typical rinses will increase from 40-500 mg/l NaCN up to about 2000 - 3000 mg/l NaCN. Chlorination of these more concentrated rinses requires that extreme care be taken to avoid the release of a chemical intermediate, highly noxious cyanogen chloride gas. There is thus a need to demonstrate a process that does not have the potential for producing this intermediate in the treatment of concentrated cyanide rinses, and which allows simple recycle of the resultant metal precipitate.

To briefly summarize, a cyanide zinc rinse containing typically 500-5000 mg/l NaCN is first treated at up to 104°F (40°C) for about 1 hour using roughly equimolar quantities of formalin (37% solution of formaldehyde) and Kastone[®] peroxygen compound (Reg. U. S. Pat. & tm. off., DuPont Company), a specially formulated peroxygen product containing about 41% hydrogen peroxide and special stabilizers and flocculants. During treatment, free cyanide is converted to a mixture of ammonia, sodium cyanate, and glycolic acid amide, and concomitantly the zinc ion is precipitated as zinc oxide. The zinc oxide sludge can be removed by settling without the use of added polyelectrolyte, and can be filtered to yield a high solids sludge, e.g., containing up to 20% by weight of zinc (calc. as Zn). The sludge is then dissolved in a quantity of plating solution, and the resulting solution, after filtration to remove any insolubles, is fed to

the original cyanide zinc plating bath.

Metal Plating Corporation obtained provisional permission to operate the DuPont Kastone® system from the Indiana State Board of Health in March 1973. The company went on stream in June 1973, obtained the grant for this demonstration project effective July 1974, and started recycling sludge in November 1974. From March 1973 to November 1974, some 53-55 gal drums of precipitated zinc plus calcium and magnesium sludges were accumulated; since the advent of recycling, no more has accumulated. The operation of the Kastone® system has been successful. About 1100 gal (4164 l) of rinse water is pumped to the treatment system. Approximately 1000-3000 mg/l of NaCN was reduced to 1.0 - 7.0 mg/l NaCN, the latter analyzed by total distillation. The treated solution contains <.25 mg/l free NaCN. Analyses of total plant effluent indicated <1.0 mg/l NaCN (by total distillation). Examples of treatment are indicated in Tables 1 and 2.

Since this is the first project of this sort to attempt zinc sludge recycling, there were several unknown parameters that had to be estimated. The first parameter was the size of any filters used. It became quickly evident that the initial filter was too small. The second parameter was how well the sludge would concentrate. The third was how much any insolubles would interfere with the recycling. Fourth, would the return of any breakdown products from brighteners, cyanides, and formaldehyde interfere with the plating bath? Other returned (recycled) impurities would be copper and ferrocyanides. Would these have any accumulative effects?

The one problem area in the process that needed to be overcome was the labor intensive aspects of the recycling. This in itself is basically a matter of design and sizing of the filtration unit for concentrating the zinc sludge. Currently it takes about 3 hours of direct labor to accumulate the sludge. A reduction in the amount of chemicals that require treatment can reduce the volume of sludge to be handled and thereby reduce the time required to handle the resultant volume of sludge. A secondary benefit of reduced treatment costs can also be realized. This has been indicated by experimenting with a drip station before the first rinse tank after plating.

TABLE 1. EXAMPLES OF DAILY TREATMENT a,b,c,d

Date	NaCN (mg/l)	Orig. pH/ Adj. pH	Additions			Final	
			NaHCO (lb)	HCHO (gal)	Kastone® (gal)	pH	NaCN ^f (mg/l)
14Nov74	2511 ^e	12.4/10.6	40	3.0	6.0	10.4	2.0 ^{e,g}
27Nov74	1480	12.5/10.6	40	3.0	5.0	10.1	5.8
02Dec74	2381	12.8/11.4	50	5.0	6.6	10.2	1.2
13Dec74	1795	12.9/10.7	40	3.0	5.0	10.0	5.8
27Jan75	2871	12.9/11.6	40	4.0	6.6	10.8	3.2
19Feb75	3365	12.8/11.3	40	5.0	7.0	10.7	7.8
27Feb75	775	12.0/11.5	20	2.0	3.0	10.5	3.2
10Mar75	3665	13.2/11.2	60	5.0	7.8	10.6	3.4
27Mar75	578	12.4/10.6	20	1.0	2.0	10.2	1.8
15Apr75	2156	12.9/10.6	40	3.0	4.4	10.1	.76
08May75	1646	12.4/10.4	40	2.0	4.0	10.2	1.6
16Jun75	2372	12.1/10.4	40	4.0	6.0	10.2	2.0

- a Volumes treated ranged from 960 to 1200 gal.
- b Temperature change was due to heating ranged from 18 to 25°C initially to a final temperature usually 29-41°C, and volumes ranged from 960 gal to 1200 gal.
- c Reaction time is at least 1 hour. There are occasions where up to 1½ hours were needed to get reaction temperature up to 40 C.
- d Settling times are usually 2 hours.
- e Samples were taken directly from the treatment tank.
- f Free NaCN <.25 mg/l (Appendix 5).
- g NaCN in the last column is total NaCN by distillation. (Appendix 5).

TABLE 2. EXAMPLES OF TOTAL NaCN IN THE PLANT EFFLUENT^{a,b,c,d,e}

Date	Total NaCN ^d by distillation
20Jan75	.45 mg/l
27Jan75	No Analysis ^e
19Feb75	.35 mg/l
27Feb75	.45 mg/l
10Mar75	.35 mg/l
27Mar75	No Analysis
15Apr75	.32 mg/l
08May75	No Analysis
16Jun75	1.2 mg/l

- a These data are generally consistent with the bulk of the data accumulated.
- b The samples are taken from a manhole access situated at the intersection of 17th and Georgia Streets, southwest of the plant. Another plant's effluent gets into our effluent and somewhat affects our analysis by dilution. This effect can be minimized but not altogether eliminated.
- c The samples are taken during time of discharge of treated supernatant to the sewer.
- d Free NaCN is generally <.125 mg/l (Appendix 5).
- e The dates on which there is no analysis are days when it rained. The storm sewer and sanitary sewer are one, and massive dilution occurs.

SECTION II

CONCLUSIONS

After investigating different types of recycling utilizing a pilot process, it was concluded that recycling of zinc oxide sludge following treatment of cyanide-zinc-bearing rinse waters is feasible with the following qualifications:

1. Equipment should be scaled up and designed to minimize labor.
2. Sludge generated is best handled on a day-to-day basis versus weekly accumulation.
3. Bag type filtration is the better of the two types of filtration tested. This is not an endorsement or criticism of the particular makes employed. The bag type filter was simply easier to operate.
4. Dragout should be minimized by using dragout stations where feasible, or use other methods to minimize dragout such as air knives.
5. Slightly lowered anode usage was observed in the reclaiming process. The lowering of the usage was in the range of 10% - 30% depending on bath formulation and eventual transportation to landfill are taken into account, the savings become significant enough to warrant a positive attitude toward recycling.
6. Secondary insolubles create some sludge handling difficulties. However, treated water (i.e. softening) eliminates these insolubles. Should the insolubles enter the plating tanks no apparent plating problems occur.

The mentioned insolubles result from the formation of calcium and magnesium hydroxides in the cyanide treatment process. These precipitates are gelatinous in nature and are inherently hard to filter out completely. Waters found in Indiana ordinarily contain 250 - 350 mg/l of total calcium and magnesium. This translates to 3.0 - 3.5 lb (1.36 - 1.58 kg) of these hydroxides in the sludge. They also constituted 30% - 40%

of the volume of the sludge handled. Some insolubles come from the Kastone[®] formulation; but these are on the order of only 10% of the total insolubles coming from the hardness in the water itself.

At the beginning of the recycling project both tanks had 27 anodes (baskets and zinc ball anodes) on 3 anode bars. The bars split the 1400 gal plating tank into 2 stations. Zinc content in both baths rose from about 4.0 oz/gal (30 g/l) to near 5.0 oz/gal (37.4 g/l) and NaCN was raised accordingly (NaCN:Zn ratio was kept near 2.8:1 to 3.0:1). By placing steel anodes so that each bar had 5 zinc anodes and 4 steel anodes (15 total and 12 total zinc and steel per tank) the zinc metal content was reduced to about 4.0 oz/gal (30.0 g/l) zinc. Currently the following anode composition is being used - 18 zinc anodes and 15 steel anodes per tank. Each bar contains 6 steel and 5 zinc anodes equally spaced and placed - zinc - steel - zinc - steel, etc.

This has resulted in some savings in anodes. The recycling in the experimental tank appears to have offset some zinc anode useage also. The "fine tuning" of the plating bath anode composition resulted in stabilizing the zinc content near 4.3 - 4.5 oz/gal (32.2 - 33.8 g/l). Zinc ball anode consumption was reduced by about 30% at most. On the average, the control tank took 35 lb/day of zinc ball anodes.

Reduction of the amount of cyanide treated is economically advantageous. A drip station was used for a limited time. The initial data, though not conclusive indicates a reduction of approximately 50% of dragged out cyanide and subsequent treatment.

The main advantage to recycling of sludge is primarily economical. Equipment can be amortized, whereas the aforementioned accumulation storage and transportation are simply ongoing costs. As indicated the project was set up as a pilot project and proper scaling of the equipment becomes imperative to minimize labor.

A general layout and overview of the equipment utilized to date is given in figures 2 and 3, Appendix 1.

ECONOMICS OF RECYCLING

1. Daily Treatment Costs (Cyanide converted to Cyanate):

Chemicals

3.0 gal Formaldehyde, 28.8 lb @ \$.094/lb.....	\$ 2.71
5.0 gal Kastone [®] , 500 lb @ \$.245/lb.....	12.25
40.0 lb Sodium Bicarbonate, 40.0 lb @.....	3.00
	<u>17.96</u>
Labor, 2 hours @ \$5.00/hr.....	10.00
TOTAL	\$27.96

This cost is ongoing whether or not recycling is accomplished and does not include investment in the equipment required to treat (treatment tank, console, plumbing, or pumps). The above chemical cost is based on 1800 ppm NaCN maximum, which is the current maximum dragout of NaCN.

2. Daily Recycling Costs

Labor, 3 hours @ \$5.00/hr..... \$15.00

To reiterate this labor is directly associated with the filtration process and is the main reason for wanting to mechanize it more.

3. Daily Saving of Zinc

Dragout of Zinc (approx 700 mg/l) 7 lb @ \$.70/lb....	\$ 4.90
Zinc Ball Anodes 10 lb @ \$.70/lb.....	7.00
Total	<u>\$11.90</u>

4. Daily Cost to Store and Transport Zinc Sludge

Labor (to accumulate sludge), 2 hours @ \$5.00/hr.....	\$10.00
Transportation of Sludge.....	8.45
Total	<u>\$18.45</u>

The cost of transportation was based on the year's accumulation (prior to recycling) of 53 drums of sludge and a Quote from a local firm of \$40.00/drum to take to a land-fill. Using a 250-day year, one obtains \$8.45/day for hauling expenses.

Comparing points 2 and 4 even though the 3 hours of labor can be minimized, it is still more expensive for Metal Plating to store and transport sludge. Then added to that is the lost value of the zinc which would bring the total cost of this way of handling sludge to \$31.05/day. Point 2 is based on the current filtration practice which is soon to be alleviated via larger filtering capacity.

To date there has been an outlay of \$10,600. in equipment only for treatment and recycling (treatment - \$4,800 and recycling \$5,800). Investment in a larger filter will bring the outlay to \$12,800. Using this last figure and a 5 year amortization gives \$2,540/year or \$10.16/day in investment. This translates to \$4.53/day investment to treat and \$5.53/day investment to recycle.

SECTION III

PROCESS DISCUSSION

Since this project is rather new and no previous experience (in this particular area) exists to rely upon, it is necessary to draw upon information from various resources, and arrive at some conclusions as to the nature of the dissolution of zinc oxide. The ions $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{CN})_4^{2-}$ are considered to be the predominant species existing in zinc cyanide plating baths. The tetracyanide ion is believed to predominate over the zincate ion as cyanide tends to form stronger bonds with transition metals than does hydroxide. Since the starting material is ZnO (or possibly $\text{Zn}(\text{OH})_2$ in the presence of water), the following mechanism for dissolution was proposed. Sludge will be mixed with plating solution having the following approximate composition NaOH -10.0 oz/gal (75.0 g/l), NaCN -13.0 oz/gal (97.5 g/l), and Zn -4.0 oz/gal (30.0 g/l). This represents approximately .45 molar Zn and 1.9 molar NaCN or CN^- .

REACTIONS

1. $\text{ZnO}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Zn}(\text{OH})_2(\text{aq})$ in the presence of excess OH^- . Reference: Andrews, H. A. and Kokes, R. J.: Fundamental Chemistry, 2nd ed.: Wiley and Sons, 1965: pp 425-426.
2. $\text{Zn}(\text{OH})_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_3^- (\text{aq})$
3. $\text{Zn}(\text{OH})_3^- (\text{aq}) + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-} (\text{aq})$

However, the presence of cyanide probably replaces the hydroxide after initial hydration and the following probably occurs:

4. $\text{Zn}(\text{OH})_2(\text{aq}) + \text{CN}^- \rightleftharpoons \text{Zn}(\text{CN})\text{OH}(\text{aq}) + \text{OH}^-$
5. $\text{Zn}(\text{CN})\text{OH}(\text{aq}) + \text{CN}^- \rightleftharpoons \text{Zn}(\text{CN})_2(\text{aq}) + \text{OH}^-$
6. $\text{Zn}(\text{CN})_2 + 2\text{CN}^- \rightleftharpoons \text{Zn}(\text{CN})_4^{2-} (\text{aq})$

Since apparently 4 moles of CN^- are tied up with 1 mole of Zn^{+2} the plating bath with .45 molar Zn and 1.9 molar CN^- would have, by calculation, .1 molar CN^- left over to react with ZnO sludge. Assuming 20% Zn is in the concentrated sludge, this would be equivalent to .2 lb (approx. 1.35 moles) Zn . Further calculation yields approx. 16 gal (60.5 l) of plating solution necessary to dissolve 1 lb (2.2 kg) of sludge.

The one conclusion drawn was that a fairly large volume of plating solution is required to redissolve a relatively small amount of sludge. The other supposition to be made is that sodium cyanide should be added to aid dissolution of the sludge. This will be touched on later. It should also be considered that some agitation and possible steam heat be admitted to aid dissolution as well.

These items were taken into consideration in the design of the secondary settling tank (see Appendix 1). It was scaled to a 300 gal volume. However, the selection of the return cartridge-type filter was done on a relatively arbitrary basis for this pilot project. The immediate impact was the fact that it was too small. The bag type filter which was supplied to Metal Plating for evaluation is also too small. Both filters had a tendency to allow slippage of insolubles through to the plating tank. This was also attributed to each being pilot sized. A difficulty which arose was the inability to wash out cyanide from the cartridge-filter completely before stripping it down. The bag type filter did not present these problems. However, as stated both were too small for the volume of sludge produced. The bag type filter had a definite advantage in being able to clean out accumulated sludge easily thereby minimizing labor.

The primary intent of this investigation was to accumulate sludge on the filter, and then redissolve it by recirculating plating solution through the filter. The filter would retain insolubles. Since the filters were too small, the next most probable approach was to use the filters to concentrate the sludge. The sludge would be transferred back to the secondary settling tank. NaCN, plating solution, heat and air would be applied, and the resulting solution would be filtered back to the plating tank. However, the insolubles became a significant factor. They are primarily calcium and magnesium hydroxides ($\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$). Most of the Ca and Mg come from using hard water in the rinse system. Kastone® simply adds a little more solids. The total effect is the equivalent of 2 lb to 2.5 lb of Ca and Mg. $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are not redissolved by NaCN. Also some Ca and Mg may be in the form of CaCO_3 and MgCO_3 , as NaHCO_3 is used in the destruction of CN^- . These precipitates are gelatinous and plug the filter. Some of the precipitates pass through the filter as previously mentioned. In practice this "secondary sludge" has to be handled. Admission of this material to the plating tank does not seem to adversely effect the plating quality. The loose flocculent material is readily resuspended, but does not appear to cause shelf roughness and, as such, can be tolerated in the plating bath. However, in the overall picture, it is not advisable to operate a plating bath with foreign material present. More frequent desludging of the plating bath may also be necessary, and downtime, labor and disposing of the extra sludge that results are extra expenses that are basically undesirable.

Elimination of Ca and Mg by softening is currently being employed. Some reduction of the volume of sludge handled is the first benefit noted, and there has been no build up of insolubles. Handling of the resultant zinc sludge has not been minimized. However, keeping in mind the pilot nature of the process, simple scaling up of the filtration will eliminate all unnecessary handling.

SECTION IV

PROPOSED METHOD OF RECYCLING AND GENERAL PROCEDURE

From the information and experience gained by operating some types of recycling (Appendix 3), the following method has been abstracted, and is considered to be the most promising and least labor intensive (and therefore desirable) method of recycling. Once treatment and primary and secondary settling have taken place, the sludge is further concentrated and collected on a battery of pressure filters. Excess supernatant is discharged to the sewer. Plating solution is then recirculated through the filters dissolving the zinc sludge. Once dissolution is completed the filtering system is blown clean again to eliminate cyanides from this portion of the system. The water used is sent to treatment. This completes the process and the system is ready for the next treatment.

The equipment proposed is described in figure 1 and is scaled up per Appendix 2. The sludge from the secondary settling tank is concentrated on filters a, b, c. and d, shown in figure 1, and eventual recirculation of plating solution then dissolves the sludge.

COLLECTION OF SLUDGE:

Valves 1, 5, 6 - 13, 17 and 18 are open. All others are closed. The sludge is then filtered and recirculated to and from the secondary settling tank, and once a clear supernatant is observed, valves 17 and 18 are closed and valve 19 is opened. This then eliminates the final volume of treated supernatant and delivers it to the holding tank for discharge to the sewer.

AIR PURGE:

Sludge is concentrated on the filters. Valve 5 is closed and compressed air is admitted to the filter chambers through the air ports, and filter chambers are purged of any final volume of supernatant.

RECIRCULATION:

The line from the plating tank is primed by admitting water (either city or softened) through valves 2 and 13 then closing 2. Valve 5 is opened and 19 is closed. Valve 15 is then opened and the pump started. Plating solution then circulates to and from the plating tank through the filter. This is continued for about one hour or until visual inspection of a given filter

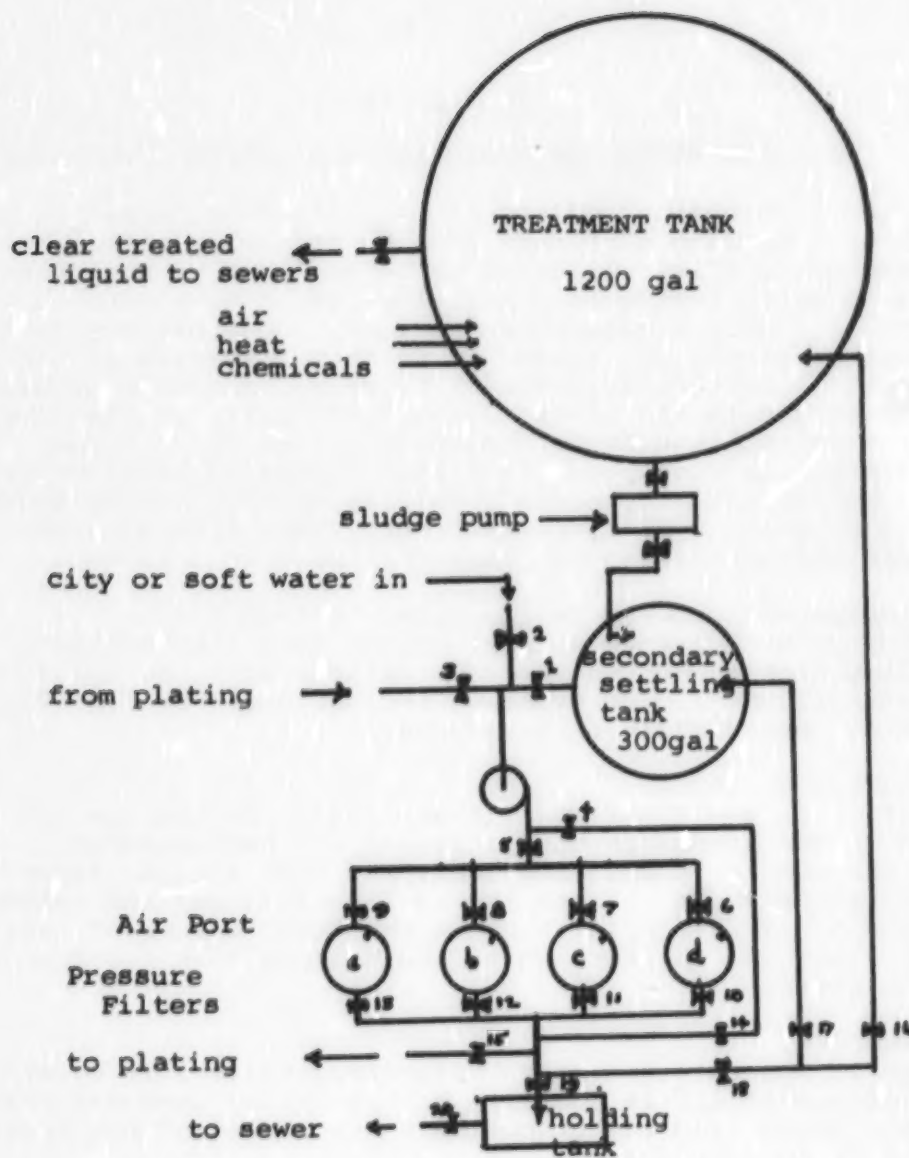


Figure 1 Proposed Treatment and Recycling System.

indicated dissolution is complete.

AIR PURGE

At this point valves 3, 5, 6 -13, and 15 are open. All others are closed. Valve 15 is closed and air is admitted as before through the ports on the filter chambers. Plating solution is blown back to the tank clearing the inlet line and pump. Valves 3 and 5 are closed. Valve 15 is opened and the air is applied through the chambers and the outlet line from the filtering system. Valve 15 is then closed.

WATER-AIR PURGE

Valves 6 - 13 are opened. All others are closed. Valves 2, 3, 5, 18 and 16 are opened and the system filled with softened water. Valves 2, 10 - 13 are closed and valves 4 and 14 are opened. Air is admitted as before clearing the inlet side of the filters, and pushing the cyanide contaminated water to treatment. Valves 4, 5, and 14 are closed, and valves 10 - 13 are cleared of cyanide contaminated water sending it to treatment. All opened valves are now closed and the system is ready for new sludge.

The main reasons for clearing the lines to and from the plating tanks are (1) standing air in the lines prevents possible siphoning of solution from the tanks (in case of a leak) and (2) solution standing in pipes has a tendency to "creep out" through joints and unions even though tightening appears to be sufficient. PVC could be used and all joints glued to prevent creepage. However, PVC also presents a problem of its own fragility. All of the foregoing then is a representative of a relatively full scale system for the recycling of zinc sludges and the volumes and sizes recommended should be considered minimums. Items not shown in Figure 1 are catch pans under the pump and filters (to catch any small spillage of contaminated water), and the console unit which meters formaldehyde and Kastone®. These were deleted for the sake of simplicity. The overall system treatment and filtering can be set in an area approximately 16' x 9'. Softened water be preferably used to flush out the system (water purge) but municipal water could be used. The basic idea is to keep calcium and magnesium from hard water to an absolute minimum so as to minimize their influence. The foregoing, then, would be considered as a complete recycling system for a 1100 gal rinse system which would have a total of 1000-3000 ppm of NaCN dragout with the corresponding 370-1110 ppm Zn.

SECTION V

APPENDICIES

APPENDIX 1. EQUIPMENT LIST AND FIGURES SHOWING APPROXIMATE LAYOUT OF EQUIPMENT

1. March magnetic pump, centrifugal, Mod. No. TE-7R-MD
2. Treatment tank, 6' dia x 6' with 1' deep conical bottom, 1200 gallon
3. Platecoil, steam coil, 2' x 1½' (in treatment tank)
4. Airsparger (in treatment tank 4' x ½" pipe with holes on 6" centers)
5. Sludge pump, Texstream, TD 390
6. Control Console, Lenape Engineering, with 2-0.4 gpm metering pumps
7. Industrial filter 1800 gph, 6 - 29" cartridges
8. Transfer pump, centrifugal TENV motor, Industrial Plastics 1800 gph
9. Secondary Settling Tank 3'7" dia x 4' with 6' deep conical bottom - approximately 300 gal capacity
10. Serpentine steam coil (4 loops - 2' lengths of ½" pipe) (in Secondary Settling Tank)
11. Airsparger (in Secondary Settling Tank 3 x ½" pipe air filters on 6" centers)
12. Sethco SS-1200 cartridge filter
13. Gaflo, Pressure filter, Mod. RB-1A (This is currently Mod RB4A which has four times the filter capacity)
14. Fittings and pipe, 1" black iron
15. Valves, 1" PVC (for recycle portion)
16. Holding tank 100 gal

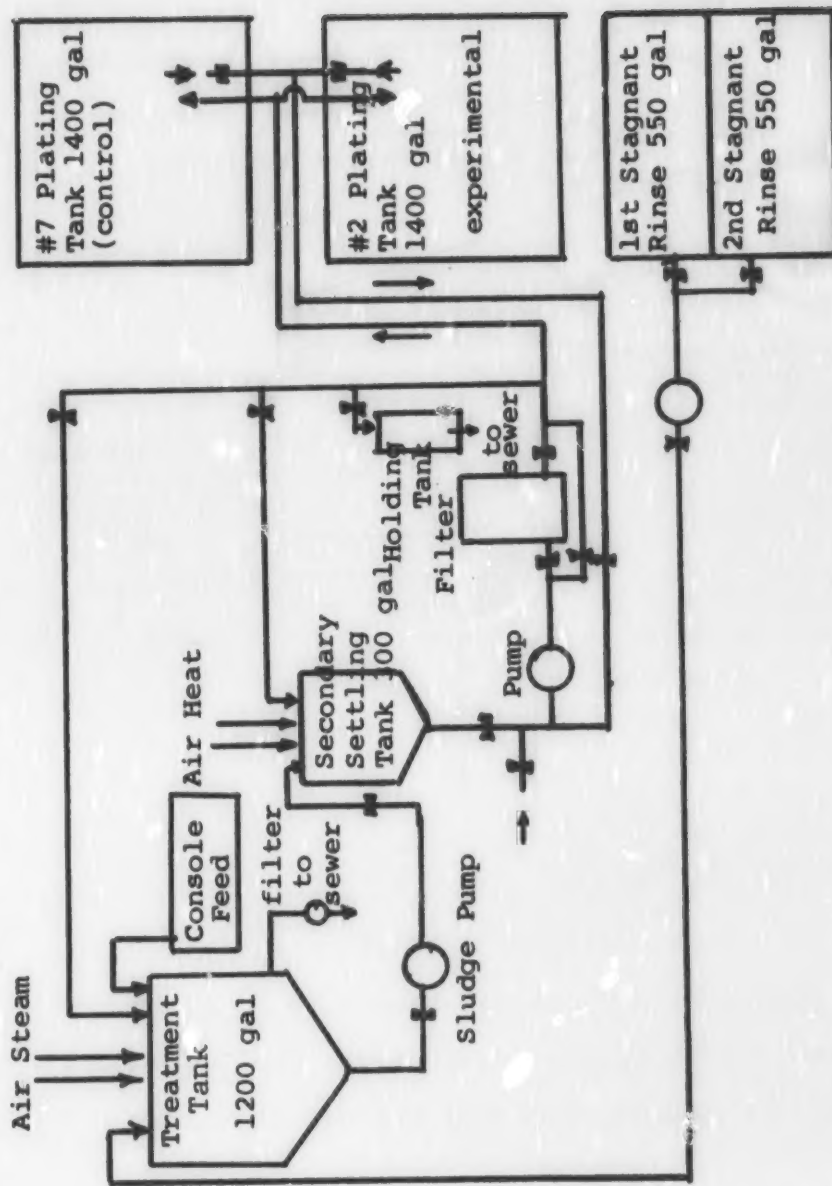


Figure 2. General layout of treatment and recycling equipment.

3. Settling
This does take 2 hours to accomplish for this installation and there appears to be no other means of speeding this up. The main problem was the sludge became more gelatinous, and harder to handle in the final filtering prior to redissolving when a polyelectrolyte was added to increase settling rate
4. Decant
Using the polishing filter reduces the discharge time to 1 hour versus 2 hours of gravity flow discharge. However, larger ports and lines from the treatment tank would speed up both. At the time of this writing the polished filter is used as needed when the supernatant is not clear to a depth of 6' (see Appendix 1 dimensions of treatment tank).
5. Pump Sludge to Recycle
This is only 10 to 15 minutes at the very most since only 70 to 90 gallons of "boot" is left after decanting about 1100 to 1200 gallons of supernatant.
6. Settle and Decant
Once the sludge in the "boot" has been pumped to the secondary settling tank it is allowed to resettle and usually 50 to 60 gallons of clear liquid are decanted again. This reduces the total amount of sludge to 30 to 40 gallons. This last volume is dependent on the total amount of dragout initially treated.
7. Filter and Concentrate Sludge
Metal Plating purchased a Sethco filter. As it turns out this filter is too small to adequately handle all the sludge involved. A GAF bag filter was obtained and evaluated. Its use resulted in reduced handling and operator time. It, however, is also too small and should be 3 to 4 time larger, as should be the Sethco unit. The sizing up of the filter will make a simple single pass filtration possible and eliminate the need for changing filter bags or inserts. This will allow simple accumulation of sludge on the filter and subsequent recirculation of plating solution through the filter.
8. Redissolve Sludge and Return to Plating Tank
Since the zinc baths are operated at room temperature and since dragout of water from prior rinses about equals dragout of plating solution, there is little loss of volume from the plating tanks. This makes reduction of volume of returned sludge quite critical. To be explicit, the return volume for this specific situation is 15 gallons (57 l) maximum per day. The accumulated sludge is placed in a 30 gallon barrel; plating solution added; this is slurried; and then added back to the plating bath. If the filter noted in the previous step were large enough the sludge could be accumulated thereon and redissolved by simply

recirculating plating solution through the filter and returning it to the plating tank.

These last steps require more close personal attention. To summarize, operator time is the most important element involved and these last steps are the most labor intensive. The single item of most importance to recycling is the filter which should be 8.4 sq ft (.78 Sq M) for 1000 to 2000 mg/l of NaCN or 330 to 670 mg/l of zinc precipitated as zinc oxide sludge.

APPENDIX 4. TYPES OF RECYCLE OBSERVED

The first but not necessarily desirable approach taken would be considered the quick and dirty method. This worked fairly well with the exception that there was extra liquid volume which needed to be handled.

PROCEDURE

1st day 1. Treat rinses and settle sludge; decant supernatant.

2. Pump sludge to secondary settling tank and let settle overnight. (approx 90 gal or 340 l)

2nd day 1. Decant supernatant.

2. Pump sludge (20 - 40 gal or approx 76 - 150 l) directly to plater without any treatment.

This method at first looked somewhat attractive, and in a few respects remains so. The method is direct, simple and requires an absolute minimum of attendance and handling. The main problem is that with a room temperature plating bath dragout of water just about equals or exceeds dragout of plating solution. For the operation at Metal Plating this results in a volume loss of about 15 gal (57 l). Typically, there were about 30 gal (114 l) of sludge. This sludge was usually 4-5% by weight solids and it resulted from treatment of rinse waters bearing 2000-2500 mg/l NaCN. This translates to about 750-850 mg/l of zinc metal. Based on volume of rinse water and concentration we get:

1. 750 mg/l Zn = .75 g/l = .1 oz/gal
2. 1200 gal x 1 oz = 120 oz Zn = 7.5 bl

1. 850 mg/l Zn = .85 g/l = .113 oz/gal
2. 1200 gal x .113 oz/gal = 136 oz Zn = 8.47 lb Zn

This gives rise to an almost direct simple relation that every 100 mg/l approximately equals 1.0 lb Zn or NaCN in 1200 gal. This will help to simplify future calculations, (i.e. 2500 mg/l) NaCN = 25 lb NaCN also).

Also, since Zn is in the form ZnO (reference: "A Peroxygen System for Destroying Cyanide in Zinc and Cadmium Rinse Waters", Lawes, B.C., Fournier, L.B. and Mathre, O.B. (Paper presented at 48th Annual Technical Conference, American Electroplaters Society, Buffalo, New York, June 15, 1971.)), there is 1.25 lb ZnO for every 1.0 lb Zn. Thus 7.5 lb Zn becomes 8.4 lb ZnO and 8.5 lb Zn becomes 10.1 lb ZnO. Since, the sludge is in 30 gallon (approx 250 lbs) water, the ratio of ZnO to water approximates 3.4-4.0% by weight solids. Add to this the other insolubles and 4-5% by weight solids results. This appears to be a maximum value obtainable by settling alone. Thus, other means (i.e. filtration) are needed to effectively concentrate the sludge further and reduce overall volume of the sludge. Since this simplistic approach gave too much volume to handle, other approaches were evaluated. There was at least 15 gal (57 l) per day extra volume that was decanted from the experimental plating tank to the nearby barrel line plating system in order not to have a few drums of solution standing around. Operation of this method occurred in January 1975. There were a few tentative trials in December 1974 once all equipment was hooked up.

Possible solutions to the problem encountered while trying this method could be:

1. Warm plating baths to get evaporation and volume loss.
2. Reduce drag-in of water from previous rinse so that (drag-in < drag-out) volume loss occurs in plating baths.
3. Evaporate excess volume of sludge.
4. Filter off excess volume.

The first possible solution gives some changes in the plating baths which are undesirable to Metal Plating. As such this solution was abandoned. The second solution was deemed unfeasible but was not tried. The third solution was tried with some success. However, ammonia fumes are given off rather profusely (refer to above reference by Lawes, Fournier & Mathre) at 40-50°C while heating at that temperature for several hours to get about 15 gal (57 l) volume loss in the sludge. Venting of ammonia was not available and this approach was abandoned. Thus the most favorable approach at the moment appears to be filtration after settling. Combinations of the foregoing solutions were not tried. The basic format to this particular type of recycling would be to (a) force a volume loss in the plating bath and (b) concentrate sludge as simply as possible, then recycle to the plater.

This type of recycling does give rise to some other problems.

1. Organics are returned. This gave rise to a cathodic film on the parts (from the experimental tank) which was hard to remove in the nitric rinse. Subsequent

permanganate treatment of the plating bath eliminated this problem.

NOTE: The direct relation of organics recycled and the film were not completely ascertained. However, since the same film did not occur in the control tank by inference the problem occurred as a result of recycling. Hull Cell tests run on both baths (control and experimental) by DuPont did not indicate organic contamination.

2. Bath dilution occurs by returning 30 gal of sludge per day and additions of NaCN become larger.

To summarize, this method of recycling is appealing because of apparent simplicity. However, the simplest method may or may not be the best. Application of volume control at the plating tank could still make this a possible method of recycling.

The second approach to recycling was a result of the conclusion to limit sludge volume. In setting up the recycling equipment a Sethco SS1200 cartridge filter was obtained. It utilized 10 micron filter cartridges. This second method would be to (a) collect sludge on the filter, then (b) recirculate plating bath through the filter to redissolve ZnO. Immediately it was found that the filter was undersized. The sludge plugged the whole filter chamber leaving more sludge in the Evaporator-Dissolver to be concentrated. Subsequently it was almost impossible to consider alternate collection and recirculation as planned. The recirculation of plating bath was tried. This met with only limited success. Apparently one of two things occurred: (a) by-passing of the filter elements or (b) the insoluble particulate matter was too small to be held by the 10 micron filter or (c) a combination of (a) + (b) occurred. This method was operated one week in February 1975 and abandoned.

Possible solutions to the problem would be:

1. Increase size of filter possible 3 to 4 times.
(Information for this will come later.)
2. Use a different type of filter.

To summarize this portion, a larger filter might work better to collect sludge but still may admit insolubles to the plating bath due to the nature of the insolubles.

The third method evaluated was the accumulation of sludge in the treatment tank over the period of a week. The sludge was then fed into the plating bath a portion at a time by redissolving in the secondary settling tank and filtering to the plating bath. The procedure was:

1. Leave sludge in treatment tank and decant clear supernatant daily.
2. At the end of the week transfer accumulated sludge to Secondary Settling Tank, and decant any supernatant.
3. The following week while more sludge is accumulating in treatment tank, return the dissolved sludge in the Secondary Settling Tank to the plating tank.
4. Return of the sludge to the plater is done by:
 - a. Pumping some plating solution 100 gal (379 l) to the Secondary Settling Tank.
 - b. Heat and air agitate to redissolve zinc.
 - c. Return through filter.

The main positive feature of this method is that it minimized labor. However, once keyed into this process it is almost impossible to switch to another process because of the volume of the accumulated sludge 120 gal (456 l). This method was operated relatively successfully from February 1975 through April 1975. The "organic problem" which occurred in the first part of recycling had not re-occurred. However, another problem had come about. This was a darkening of plating in certain parts which had areas of extreme low current density. This darkening occurred in both plating baths and as such was not attributed to the recycling efforts. Permanganate treatment alleviated this problem somewhat and tended to prove the problem was organic in nature.

In March a GAF bag type filter was acquired for evaluation. This was hooked up to the system. The new filter was used to try to concentrate the sludge further. The new procedure was:

1. Leave sludge in treatment tank; decant clear supernatant daily.
2. At end of week transfer accumulated sludge to the Secondary Settling Tank and decant any supernatant.
3. The following week use the new GAF filter to concentrate sludge and transfer sludge to drums.
4. Place the sludge back into the Secondary Settling Tank.
 - a. Pump plating solution 150 gal (568 l) to Secondary Settling Tank.
 - b. Add NaCN to aid redissolving, with air and heat.
 - c. Return to plater through new GAF filter.

The labor intensive aspects of this type of procedure can be readily appreciated. The process of filtering the settled sludge from the secondary settling tank to a more concentrated form took 4 to 5 hours of concerted effort. A larger filter could have possibly alleviated this.

Examples of concentrating sludge.

1. Volume of one weeks sludge pumped to Secondary Settling Tank - 234 gal. (886 l)
2. Volume of one weeks sludge after settling in Secondary Settling Tank - 144 gal. (545 l)
3. Volume of one weeks difference (1 +2) clear supernatant - 90 gal. (148 l)
4. Volume of one weeks sludge after concentrating in drums - 39 gal.

It can be seen that the effect of using the filter gives about a six to one concentration ($234/39 = 6.0$) and starting with 8-10% by weight solids a final value of 48-60% solids could be expected. All of this required 40-50 separate filtrations and 4 to 5 hours of labor.

A summary of this aspect of recycling would be that while the concentrating aspects were good the same insolubles problem was evident. This type of recycling was abandoned by the end of May 1975, because this method is quite labor intensive.

The fourth method of recycling was simply returning to a daily basis and applying filtration using the GAF bag type filter. The procedure was:

1. Treat rinses, and allow sludge to settle, and decant supernatant.
2. Pump sludge to Secondary Settling Tank and allow sludge to settle overnight.
3. Decant supernatant.
4. Concentrate sludge through filtration.
5. Redissolve sludge.

An example of this method would be:

Volume of boot	90 gal (341 l)
Volume of settled sludge	35 gal (132 l)
Volume of decanted supernatant	55 gal (208 l)
Volume of filtered sludge	8 gal (30 l)

As such there is a concentrating effect and this keeps the level of sludge volume less than the 15 gal dragout of volume stated in the first approach to recycling. Since the insolubles still pass through the GAF filter as seen in the third method evaluated it was decided that other methods to relieve insolubles be investigated. As such the concentrated sludge is taken to the plater in a 30 gallon drum. Plating solution is then mixed with the sludge, slurried up and poured back into the plating bath. This type of recycling has been practiced through June 1975 to the date of this writing. This method is still somewhat labor intensive as the final concentration requires 4 to 5 separate filterings and 1 to 1½ hours to accomplish those filterings. Also slurrying of the sludge and return to the plating bath requires ¼ to ½ hour of labor.

To summarize this method, it appears daily recycling of sludge is most desirable simple by keeping the total volume generated at an acceptable level (<15 gal).

The main thrust of this portion of the recycling is that at least effective concentrating of sludge is available. Labor is minimized to an extent. The method is more direct and less involved than the second approach and the third method used. Despite the insolubles problem recycling is taking place. The main point is then how to remove the insolubles effectively.

APPENDIX 5. ANALYTICAL PROCEDURES USED FOR CYANIDES

The basic procedures used are volumetric and can be found in literature such as "Standard Methods". DuPont has developed a quick test for obtaining a target concentration of sodium cyanide to be treated. This test is not to be construed as total cyanide.

Initial Cyanide (Quick Test)

1. Pipette 100 ml of cyanide bearing rinse water into a 250 ml Erlenmeyer flask. Use precautions (safety bulb) for drawing cyanide into the pipette.
2. Add 1 ml of .25% w/v p-dimethylaminobenzalrhodanine in acetone.
3. Titrate with 0.1N AgNO₃ to a salmon pink endpoint.
4. Calculate NaCN as:
 $\text{mg/l NaCN} = \text{mls of 0.1N AgNO}_3 \times 98$
5. Discussion of error: As with any experiment error begins with initial pipetting of the sample. The pipette should be 100 ml $\pm$.1 ml at 25 c, and made from borosilicate glass. The $\pm$.1 ml is predicated on a given size opening at the tip. Since cyanide solutions are caustic in nature, the tip tends to erode and widen allowing slightly faster delivery of sample. Subsequently, slightly less sample is delivered favoring lower titration and final results.

The next source of error comes from reading the burette. A 50 ml burette can be read with $\pm$.05 ml accuracy. Since two readings are needed the cumulative error is $\pm$.1 ml. For a titration on the order of 20.0 mls, the $\pm$.1 ml is the $\pm$.05% error or $\pm$ 20 ppm NaCN (approx) in the final calculation. This writer has found that the reproduceable error is

on the order of $\pm .2$ ml or $\pm 1.0\%$ (approx) for the same 20 ml titration. This translates to 40 ppm NaCN in the final calculation. In all reproducible error overwhelms the error of pipetting though erosion could lower the final results. It can be concluded that error in this test is no better than $\pm 1.0\%$ depending on the total titration.

Free NaCN (after reaction and/or in plant effluent

1. Four 400 ml of reacted rinse water (or plant effluent into a 500 ml $\pm 5\%$ Erlenmeyer flask, and add 1 ml of rhodanine (previous analysis).
2. Titrate with either .01N or .02N AgNO_3 to a salmon pink endpoint.
3. Calculate NaCN as :
 $\text{mg/l free NaCN} = \text{mls of } .02\text{N AgNO}_3 \times 2.5$
or $= \text{mls of } .01\text{N AgNO}_3 \times 1.25$
4. Discussion of error: At this point a straight forward discussion of error is not possible due to the fact that the free cyanide is generally nondetectable. That is the titration is generally .1 ml of .01N or .02N AgNO_3 which translates to either 0.125 mg/l or 0.25 mg/l respectively. At this point other influences come into play. NH_3 from hydrolysis of CNO^- and S^- which are present can use up some Ag^+ and add to the results. As such one can only report <0.25 or <0.13 mg/l NaCN. Also since the plant effluent sample is drawn from the sanitary sewer one can expect influences from possible dissolved organics.

Total Cyanide by distillation (after reaction and/or in plant effluent.

1. Assembly equipment as shown in figure 4. Adjust air flow through the gas absorber to about one bubble per second. The gas absorber has 50 ml of 1.0N NaOH in it.
2. Remove air inlet tube and add 250 ml of sample from a 250 ml graduated cylinder designed to deliver. Replace air inlet tube.
3. Through the air inlet tube add 1 ml of 68 g/l HgCl_2 and 4 ml of 510 g/l $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and mix for 5 minutes with the air agitation.

4. Through the air inlet tube add 15 ml of concentrated H_2SO_4 . The treated sample has carbonates and CO_2 will outgas upon admission of acid. Pressure can then build up rapidly forcing the solution back up and out of the air inlet tube.
5. Once the additions are mixed apply heat and reflux for 2 hours. Then remove heat allowing air to flow for another 15 minutes.
6. Remove the gas absorber from the installed equipment and wash down the connecting tube with distilled water delivering this to the absorber tube. Pour the contents of the absorber into a 250 ml Erlenmeyer flask and wash the absorber with 10 ml portions of distilled water adding the washings into the Erlenmeyer flask.
7. Titrate as before in the "free NaCN" procedure using .02N $AgNO_3$ and rhodanine.
8. Calculate total NaCN as:

$$mg/l \text{ total NaCN} = mls \text{ of } .02N \text{ } AgNO_3 \times 2$$
9. Discussion of error: Here again a relatively straight forward discussion of error is not possible. This is because H_2S and $HCHO$ are boiled over with the HCN and are captured also in the gas absorber. Both of these items directly interfere leading to higher results of NaCN.

The flow of air through the system can cause much error generally low results from either too much or too little flow. Too much flow does not allow enough time for absorption and too little flow results in not enough HCN being pulled over to the absorber. One bubble per second has been the accepted flow rate.

Taking the foregoing into account and noting the cumulative effects of sampling and reading the burette, it is then safe to say that the total error lies between $\pm 5\%$ and $\pm 10\%$. Generally, the amounts of NaCN reported in the treated sample lie between 1.0 and 3.0 mg/l and in the plant effluent between .3 and .6 mg/l.

It is to be noted here that CN^- is reported as NaCN when the species to be found in the effluent is $Fe(CN)_6^{4-}$ (ferrocyanide). Cyanide plating solutions and rinses will have ferrocyanide. The Kastone® process destroys virtually all the free NaCN and the remaining ferrocyanide is precipitated into the sludge and returned to the plating bath via recycling. Some

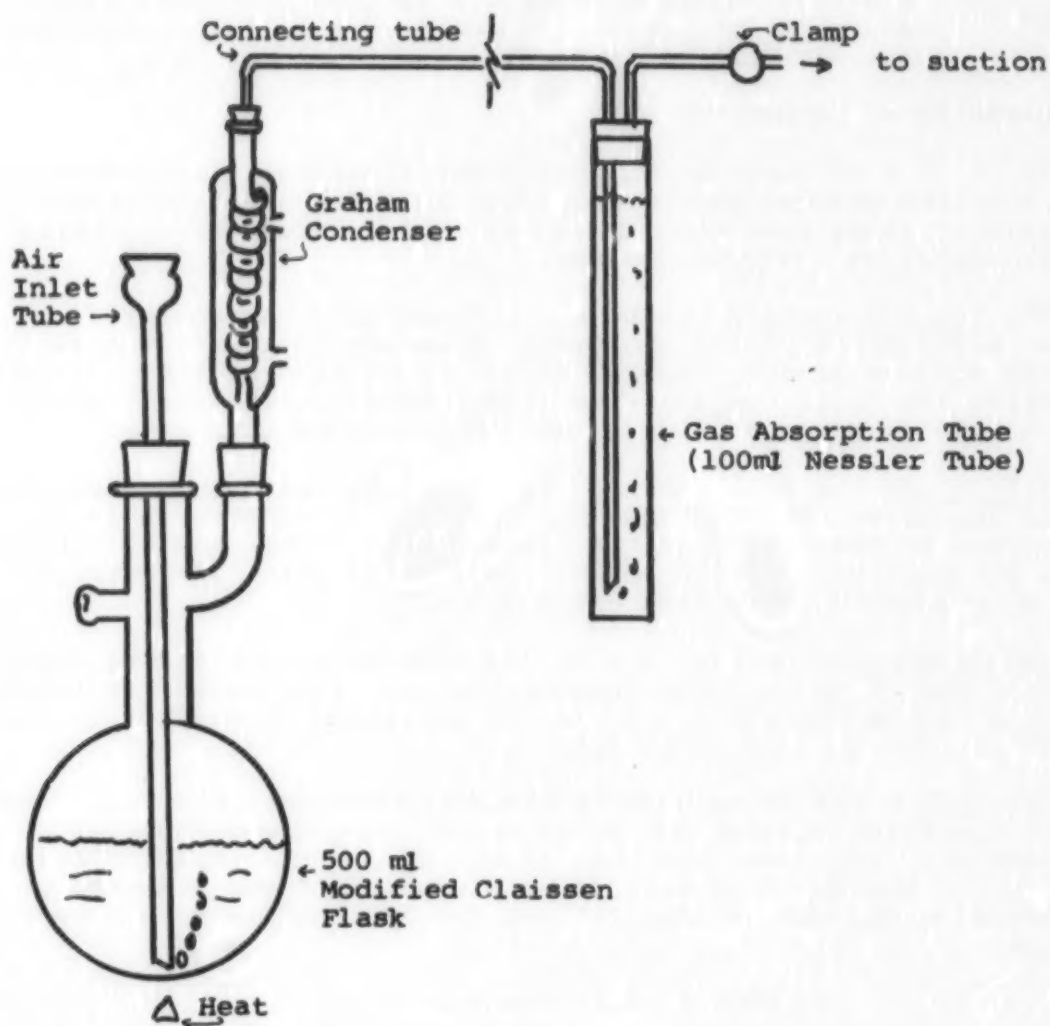


Figure 4. Total distillation apparatus

ferrocyanide remains in solution. This then is reported as NaCN.

The total cyanide procedure is that procedure currently in use by the Indiana Stream Pollution Control Board Waste Treatment Division.

APPENDIX 6. ADDENDUM

As of this writing the following modifications to the overall recycling process have been made. In reference to Appendix 2 several items have been scaled up to facilitate a more rapid treatment and recycle process.

The heating surface has been increased to an approximate 4' x 2½' plate coil (the previous onewas 2' x 1½') increasing the surface area by about 3 times. This has resulted in lowering the total heating time from 3 hours to 1½ hours, allowing the solution to heat to 45 -50°C instead of just 40°C.

Soft water has been provided to eliminate calcium and magnesium in the rinse waters. This has resulted in no observable increase in insolubles in the plating bath. This has eliminated a precipitate build up in the rinse tanks which was calcium and magnesium carbonates and hydroxides.

Larger porting on the side of the treatment tank allows faster draining of the treated supernatant once the sludge has settled. This was taking about 2 hours and now takes 45 minutes to drain the treatment tank completely.

Filtration was being done on the GAF RB-1A pressure filter, and is now being done on the RB-4A which has 4 times the filtration surface. There was too much sludge for this 3 sq ft of filtering for the RB-1A surface to handle at one time. Generally speaking the zinc sludge follows the approximate volume reduction.

80-90 gal.....Treatment boot
40 gal.....After secondary settling
6-8 gal.....After filtration (40-50% solids)

The filtration process still required 4-5 separate filtrations before the RB-4A indicating 4-5 times the filter surface will be required to entrap all solids. The current filter has 3.0 sq ft (.28 SqM) of surface. This then would indicate 12 - 15 sq ft (1.11 - 1.39 Sq M) of surface is needed. It was hoped that elimination of calcium and magnesium would drop the amount of surface needed. It is anticipated that a Gaflo RB-4A will handle all solids at this time.

What is happening is this. The micron size of the sludge is well below 25 microns, generally between 5 and 1 microns.

Initially there is a passage of sludge through the filter while the 25⁺ microns sized particles are being filtered.

When plugging of the filter finally occurs only a small portion of the sludge has been trapped. Refiltering is done in order to entrap solids as much as possible. Finer micron sizing will be employed to efficiently trap more solids. None the less a larger filtering surface will be necessary to hold the total volume of solids. Experimentation is underway to increase the particle size while treating. There are no conclusive results as yet.

Semi-automation of the pumping process from the rinse tanks to the treatment tank has been accomplished. This allows the technician on the second shift to initiate this process at the end of that shift and allow the pumping to go on unattended. Since the treatment tank is emptied out daily and can hold 1200 gal (453 l) and since the volume of rinse water is 1100 gal (4146 l) there is no chance for overflow. The pump is plugged into a timer, turned on, and left on. This was originally the initial hour of the treatment process (Appendix 3, step 1).

Note: This addendum has been added after the expiration date of the grant period. It was felt that an updating of some of the information was necessary and justified in light of Metal Plating's ongoing efforts to recycle zinc sludge.

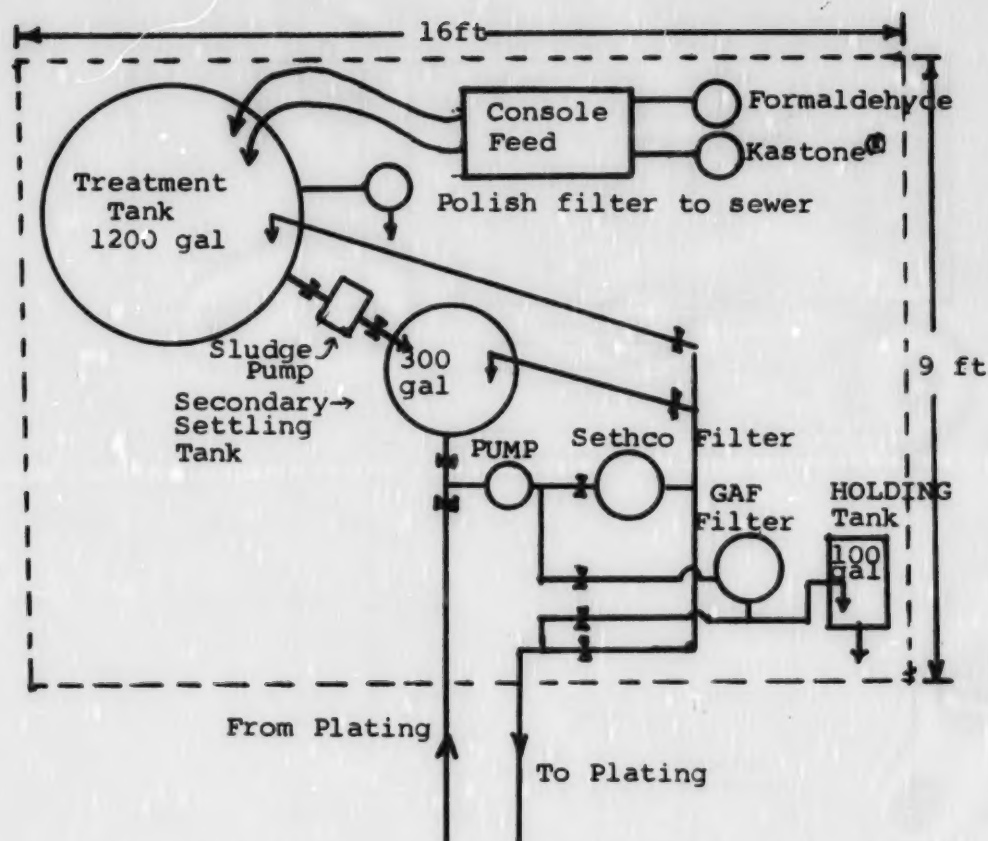


Figure 3. Approximate positions of current equipment and over all area. No attempt has been made to exact scale each item. This figure merely shows the juxtapositioning of the various elements and the plumbing to each.

APPENDIX 2. CRITIQUE AND RECOMMENDATIONS

Refer to the succeeding appendix for the particular details of the procedure used and the time element involved for carrying out this procedure. The major areas of improvement involve scaling up some of the process equipment.

1. Use of soft water for treatment.
2. Larger pump and lines going to treatment.
3. Larger heating area in treatment tank.
4. Larger ports and discharge lines on treatment tank.
5. Larger filtering surface 8.4 sq ft (.78 sq M).
There are only 3.0 sq ft (.28 sq M) now.

The main reason for scaling up is to speed up certain steps of the operation in order to minimize the time element. This will make time less of a factor in the operation and will be less critical to be sure that all steps are carried out promptly. This is not to say that the operation requires one persons full attention for 8 to 9 hours; however, a reduction of 3 to 4 hours is possible and desirable.

APPENDIX 3. DETAILED PROCEDURE FOR TREATMENT AND RECYCLING

1. Pump rinses to treatment

This involves the pumping out of 2 - 550 gallon rinse tanks and hosing out of any precipitated zinc cyanide ($Zn(CN)_2$). The actual pumpout involves 1 hour, and the hosing involves $\frac{1}{2}$ to $\frac{1}{2}$ hour. The lines and fittings from rinses to treatment are 1" I.D. The pump fittings are 1" (see Appendix 1). The improvement here would be to either gang a similar pump to the original or go to a larger pump to get about 2000 gph and utilize at least 1 $\frac{1}{2}$ " lines and fittings from rinse to treatment.

2. Analyze, add chemicals and treat

It takes $\frac{1}{2}$ hour to analyze and add the chemicals necessary and at least 1 hour after adding them to get the solution to 104° F (40° C). Here a larger heating coil is necessary on the order of 2 to 3 times as large as the current coil. This coil (Appendix 1.3) has 7.0 sq ft (.65 sq M) of surface. Steam heat is applied as soon as the coil is covered with rinse waters and the actual total heating time is 1 $\frac{1}{2}$ hours to 2 hours, leaving about 1 hour of heating to be done after addition of chemicals.